THERMORHEOLOGICAL PROPERTIES OF THE WATERBORNE ZINC-RICH COATING FROM SODIUM SILICATE SOLUTION

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The dynamic shear storage and loss moduli G' and G" of the waterborne zinc-rich coating and its binder, a sodium silicate solution, were recorded with variations of temperature and angular frequency. Results show that G' and G" initially decrease to minimum and then start to increase, while temperature ramping from 5 to 95°C. However, both the zinc-rich coating and its binder are not rheologically simple materials.

INTRODUCTION

Zinc-rich coating is an important type of primer that contains zinc pigment at concentration >80% by weight [1]. This coating usually consists of binder and zinc pigment. In search of an advanced binder material, sodium silicate solution (commercially called waterglass) shows enormous advantages, such as superior adherence and film formation, low cost [2], hard enough to withstand mechanical impact, resistant to high temperature and weather, non-flammable and smokeless in fire [3], odorless and non-toxic. These advantages, which organic resin can scarcely have, result in the suitability for the sodium silicate solution to be used as the binder of waterborne zinc-rich coating, which obeys the new VOC regulations.

As is well known, rheological phenomena are found in every coating operation. The rheological properties of the zinc-rich coating and its binder may influence their production, storage and application. Thermorheological properties correlate to physicochemical processes in the coating during the curing period. Therefore, investigation on the rheological properties of the zinc-rich coating and its binder is of immense theoretical and practical value. Previous works referring to this topic include colloid-chemical properties of zinc-silicate composition [4], influences of particle size distribution of zinc dust in water-based and structuring agent on the rheological properties of the mixed material [5,6], rheology control of nonaqueous coatings incorporated fumed silices [7], microrheological study on aqueous sol-gel process in the silica-metasilicate system [8]. To our knowledge, thermorheological investigation on the zinc-rich coating and its binder has not been reported.

The aim of this work is to measure the thermorheological properties of the sodium silicate solution and the corresponding zinc-rich coating, and then theoretically analyze the relation between thermorheological behavior and physiochemical mechanisms.

EXPERIMENTAL

Materials

The sodium silicate solution (water glass) and the zinc pigment used in this study were commercial products. The water glass has a modulus (mole ratio of SiO_2 to Na_2O) of 3.3 and weight concentration of 36 wt.%. By a spectrometer AVATAR 330, the Fourier Transform Infrared (FT-IR) spectrum for the sodium silicate solution was recorded as Figure 1. The major vibration bands are assigned as: 3600-2200 cm^{-1} the stretching vibration of –OH and HOH, 1700-1600 cm^{-1} bending vibration of HOH [9,10], 1030 cm^{-1} Si–O in-plane vibration [11], 470 cm^{-1} bending of Si–O–Si and O–Si–O [12]. An analyzer Microtrac S3500 observed the particle size distribution of the zinc pigment (Figure 2), whose average size and standard deviation are 48.8 and 13.2 μm.

Procedures

The binder for the zinc-rich coating was a sodium silicate solution diluted from the commercial water glass by the following procedure: Dilute 52.0 g water glass with 46.0 g distilled water, mechanically mix the solution until uniform, then slowly add 2 ml of modifi-

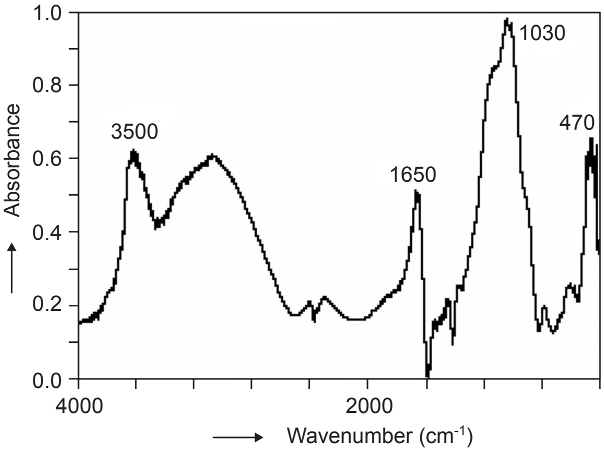

Figure 1. The FT-IR spectrum of the sodium silicate solution.

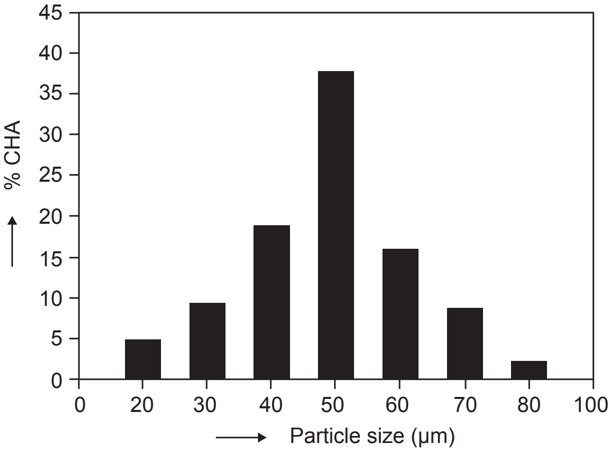

Figure 2. The particle size distribution of the zinc pigment.

Table 1. Major properties of the zinc-rich coating film.

Property	Value	Method
Drying Times	To touch ≤ 4 h, Through ≤ 24 h	GB1728-89
Adhesion	Class 1	GB/T1720
Impact	50 cmKg	GB/T1732
Salt Spray	1000 h, film completely well	ASTM B117-97
Surface current resistant rate	$10^{5}\sim10^{9}$ Ω	GB/T1410
Volume current resistant rate	$10^{5}\sim10^{9}$ Ωm	GB/T1410
Heat resistance	400°C, long term test, no damage	GB/T1735
Water immersion	3y, no damage	Direct test
Xylene immersion	3y, no damage	Direct test
Gasoline immersion	3y, no damage	Direct test

cator solution of 5 wt.% concentration under strong stirring. This yields about 100g binder with a sodium silicate concentration of 18.7 wt%.

The zinc-rich coating was prepared by directly blending binder with zinc pigment at a ratio of 1:2 by weight. Major properties of the coating film applied on the 100×50 mm sheet iron by a brusher are showed in Table 1.

For the binder solution and the coating samples, dynamic viscoelastic measurements were carried out with a rheometer AR500 (TA instruments). A standard steel parallel plate with 1000 µm gap and 40 mm diameter was chosen. The shear storage and loss moduli G' and G'' (in Pa) were recorded as functions of angular frequency from 0.1 to 100.0 rad/sec and temperature from 5 to 95°C. The oscillatory strain was 1%, which located in the linear region. The recorded data was processed by the software of TA instruments, named as the Rheology Advantage Data Analysis (v3.0.24).

RESULTS AND DISCUSSION

If a solution obeys the time temperature superposition (TTS) principle [13], the rheological problem can be simplified. Log G' versus Log G'' curves from both angular frequency sweep and temperature ramp measurements can give a clue to identify the thermorheological simple material which obeys the TTS principle [14]. Measured data over either angular frequency or temperature should form a sole curve on the LogG''-LogG' diagram for a thermorheological simple material, because G' and G'' are functions of $(a_T\omega)$ which appears as a single effective variable. Here a_T is the shift factor, a function of temperature, and ω is angular frequency. Measured data through angular frequency sweep and temperature ramp for the binder at 18.7 wt.% concentration and the waterborne zinc-rich coating are presented in Figures 3 and 4. They look rather complicated. We cannot see the fact that the data from angular frequency sweep and temperature ramp form a sole curve, therefore, neither the binder nor the zinc-rich coating should be considered as thermorheologically simple materials. Since it is well known that materials that change chemically or physically during rheological measurement will not obey the time temperature superposition principle, we propose the existence of a physicochemical mechanism in the binder and the waterborne zinc-rich coating, which is worth of deeper investigation.

Figure 5 demonstrates the dependence of G' and G'' on the temperature. It shows that they initially decrease with temperature, after dropping to minimum they start to increase sharply. We propose these phenomena to be interpreted as the combined effects of two mechanisms.

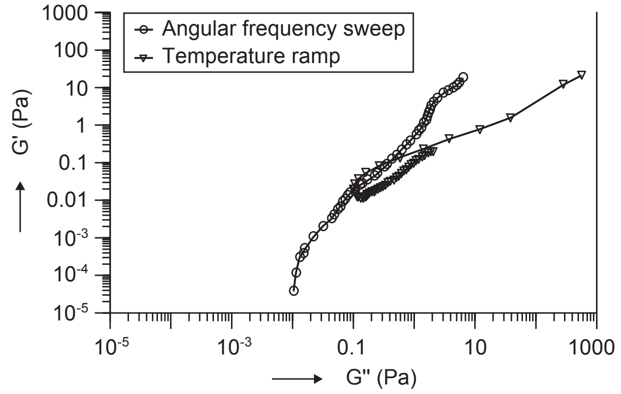

Figure 3. The Log G'' versus Log G' curves of the binder from angular frequency sweep at 25°C and temperature ramp at 1 Hz.

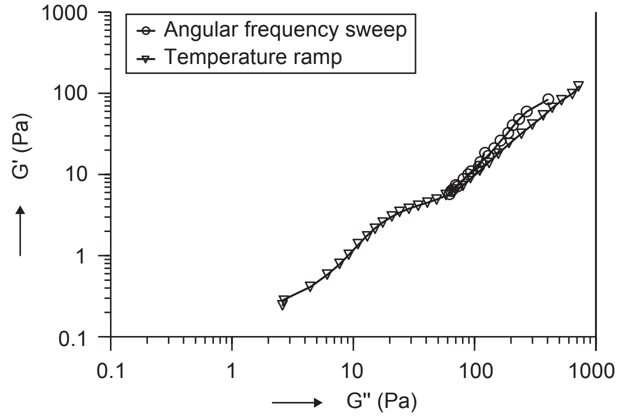

Figure 4. The Log G'' versus Log G' curves of the waterborne zinc-rich coating from angular frequency sweep at 25°C and temperature ramp at 1 Hz.

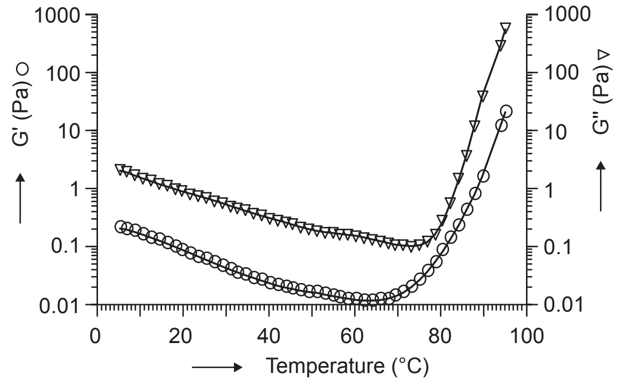

Figure 5. The temperature ramp curves of G', G'' for the binder at 18.7 wt.% concentration and 1 Hz.

The first (physical influence) is temperature that generally decreases the viscosity of most polymer solutions. Quantitatively, we propose the modulus (either G' or G'') to obey the Arrhenius relation,

$$G = A\exp(\frac{E}{k_B T}) \tag{1}$$

where A is a constant independent of temperature, E is the activation energy for flow, $k_B = 1.38\cdot10^{-23}$ J/K is the Boltzmann constant, and T the absolute temperature. It is not difficult to show that Equation (1) can properly fit the curves in Figure 5 under 70°C. The fitted values are: $A = 3.0\cdot10^{-11}$ Pa and $E = 9.5\cdot10^{-20}$ J for G', $A = 6.9\cdot10^{-5}$ Pa and $E = 4.9\cdot10^{-20}$ J for G'', respectively.

Another is the chemical crosslinking between sodium silicate molecules through dehydrolyzing reaction, which universally increases viscosity. On the base of FT-IR spectrum in Figure 1, we propose the crosslinking reaction for the sodium silicate molecules in the form of Figure 6 or the similar form to it. Below 70°C, there is scarce crosslinking in the solution, the temperature mechanism controls the process, and therefore G' and G'' decrease with temperature. In contrast, above 70°C the crosslinking effect gradually dominates during temperature increasing at a rate 5°C/min, the solution becoming thicker with time.

The temperature ramp curves of G' and G'' for the zinc-rich coating are showed in Figure 7. It is found that both G' and G'' begin to increase after dropping to minimum at ~30°C. This phenominon suggests the combined effects of temperature and chemical crosslinking also exist in the coating. However, the critical temperature of chemical crosslinking is decreased by the zinc pigment while comparing the curves in Figure 7 with Figure 5. This suggests the chemical crosslinking reaction is not the same to the case of the pure sodium silicate solution. Because of the addition of the zinc pigment, we propose metallic zinc from the surface of the zinc pigment to act as a crosslinker (Figure 8). The crosslinked reactant is insoluble zinc silicate, which fills the space among the zinc pigments with the evaporation of water, and results in the dried insoluble hard film as characterized in Table 1. Sodium ions, however, react with carbon dioxide and water to yield sodium carbonate.

Figure 9 is the measured time sweep curve for the waterborne zinc-rich coating at 1 Hz. It illustrates that both G', G'' monotonously climb up with time increasing. After ~100 minutes induction time, G', G'' of the

Table 2. Kinetic parameters for the zinc-rich coating during crosslinking process.

Moduli	t_0 (min)	G_0 (Pa)	G_1 (Pa)	k_0 (min^{-1})	E_a (J/mol)
For storage modulus	250	58.0	60.0	3.5×10^6	4.8×10^4
For loss modulus	250	62.0	55.0	2.4×10^5	4.2×10^4

coating rises more quickly. This phenominun has a plausible explanation. When the zinc pigment mixes with the binder, the metallic zinc ions from the surface of the zinc pigment start a curing process. The rheological variables increasing with time just reflect this curing process, which makes the silicates to be randomly connected through the metallic zinc and renders them insoluble. The reactant normally displays long-term stability. The bond formed can only be broken by extremely aggressive chemical action, so that an excellent inorganic zinc-rich coating film is obtained.

In order to model the evolution of the thermorheological properties as functions of time and temperature during the curing of the zinc-rich coating, we also need to know the curing kinetics. Assuming the initial reaction rate of this inorganic coating system is not zero and following Kamal's generalized expression [15], the equation for the crosslinking process of the zinc-rich coating is obtained as:

$$\frac{dx}{dt} = k(1+x^m)(1-x)^n \tag{2}$$

where *x* is the degree of conversion, *t* is the time, *m* and *n* are the reaction orders and *k* is the kinetic rate constant, which is assumed to be constant at a given temperature and to follow an Arrehenius temperature dependence:

$$k = k_0 \exp(-\frac{E_a}{RT}) \tag{3}$$

where k_0 is the pre-exponential constant, E_a the activation energy for the crosslinking reaction, *R* = 8.31 J/molK

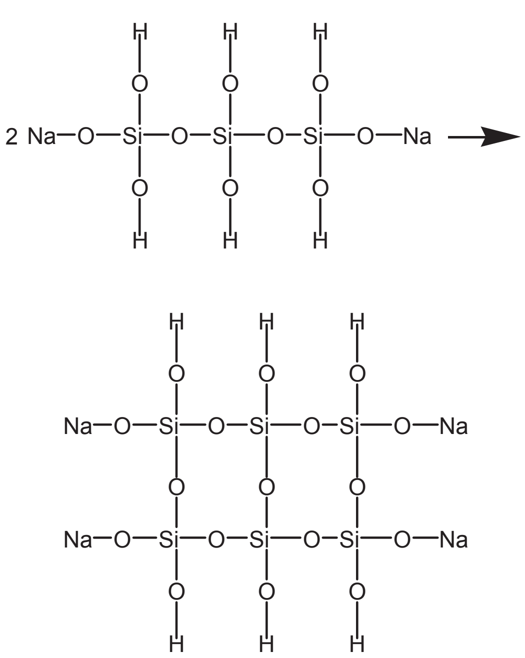

Figure 6. Crosslinking between sodium silicate molecules by dehydrolyzing reaction.

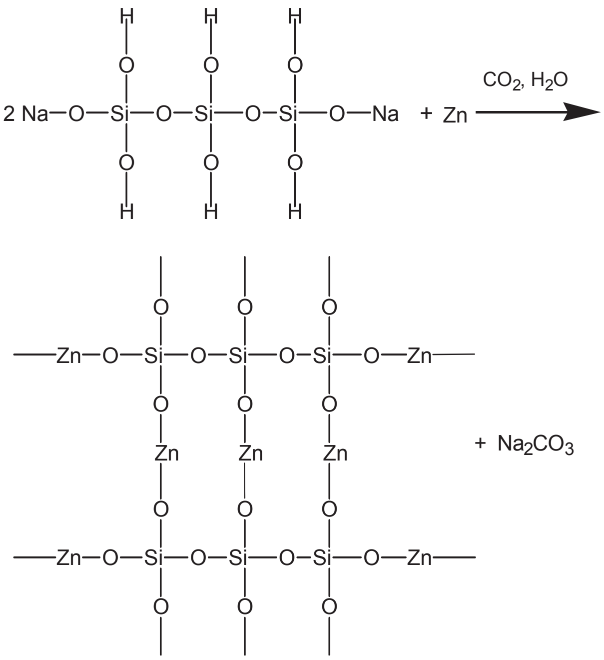

Figure 8. Crosslinking between sodium silicate molecules by metallic zinc.

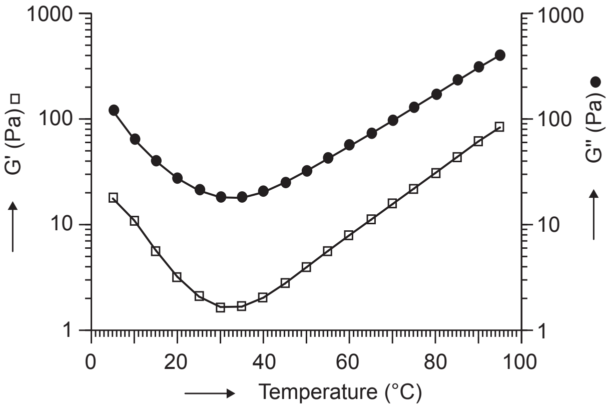

Figure 7. The temperature ramp curves of *G'*, *G''* for the zinc-rich coating at 1 Hz and 5°C/min.

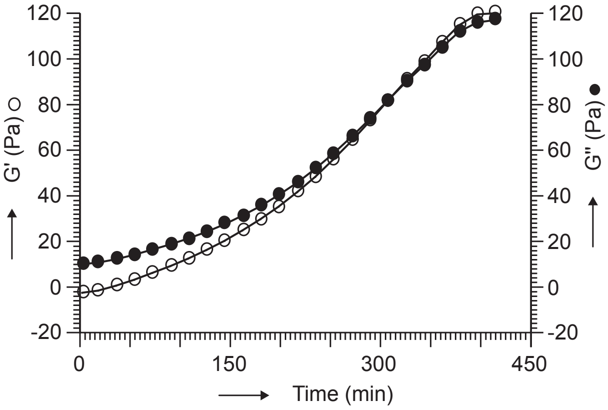

Figure 9. Time sweep curves of the *G'*, *G''* for the zinc-rich coating at 1 Hz and 25°C.

the gas constant, and T the absolute temperature. For the first order crosslinking reaction, $m = n = 1$, Equation (2) has a solution,

$$x = \frac{e^{kt} - 1}{e^{kt} + 1} \qquad (4)$$

It is clear that $x(+\infty) = 1$ as $t \to +\infty$, $x(-\infty) = -1$ as $t \to -\infty$, and $x(0) = 0$.

To correlate the conversion to the shear moduli, we assume a linear expression,

$$G = G_0 + G_1 x(t - t_0) \qquad (5)$$

where G_0 is the magnitude of either G' or G'' at $t = t_0$, $G_0 + G_1$ is the magnitude as $t \to +\infty$. After the curves in Figure 9 and data above 40°C in Figure 8 are fitted to Equation (5), results are presented in Table 2.

CONCLUSION

The dynamic shear moduli G' and G'' of a water-borne zinc-rich coating and its binder, a sodium silicate solution, were recorded by an AR500 rheometer with variations of temperature, angular frequency and time. Results show that G' and G'' mainly increase with time from 0 to 400 minutes. While temperature ramping from 5 to 95°C, G' and G'' initially decrease to minimum and then start to increase. However, the zinc-rich coating and its binder can not be considered as rheologically simple materials due to the combined effects of temperature and chemical cross linking during rheological measurement. The temperature (a physical influence) generally decreases the viscosity of most polymer solutions, and also here decreased the dynamic shear moduli of the zinc-rich coating and its binder. This process existed in the lower temperature region, and was properly fitted by the Arrhenius equation. The chemical cross linking among the sodium silicate molecules by dehydrolyzing reaction or metallic zinc increase the dynamic shear moduli. The corresponding process for the zinc-rich coating was properly fitted by the curing kinetics model, in which a first order generalized Kamal's expression was selected and the shear moduli were suggested to be linear functions of the degree of conversion.

References

1. *User guide to zinc and zinc-rich coatings for corrosion protection*, 2001/2002 TAPPI Technical Information Papers, TAPPI Press, (2001-2002) 76.
2. Polyakov S.A., Vel'mozhin S.A.: Glass and Ceramics (English translation of Steklo i Keramika) *47*, 374 (1991).
3. Gvozdeva O.N.: Stroitel'nye Materialy *4*, 33(2004).
4. Peregudova L.I., Ur'ev I.B., Izhik A.P., Akol'zin A.P.: Kolloidnyi Zhurnal *55*, 74 (1993).
5. Montes E.: J. Coatings Tech. *65*, 79 (1993).
6. Peregudova L.I., Akol'zina A.V.,. Izhik A.P, Ur'ev N.B., Akol'zin A.P.: Kolloidnyi Zhurnal *5*, 709 (1995).
7. Boothe D.P., George H.F.: Industrial Paint & Powder *70*, 24 (1994).
8. Tenan M.A., Soares D.M., Bertran C.A.: Langmuir *16*, 9970 (2000).
9. Uchino T., Sakka T., Iwasaki M.: J.Am.Ceram.Soc. *74*, 306 (1991).
10. Uchino T., Sakka T., Hotta K., Iwasaki M.: J.Am. Ceram.Soc. *72*, 2173 (1989).
11. Olejnik S., Aylmore L.A.G., Posner A.M., Quirk J.P.: J.Phys.Chem. *72*, 241 (1968).
12. Poe B.T., McMillan P.F., Angell C.A., Sato R.K.: Chem.Geol. *96*, 333 (1992).
13. Ferry J.D.: *Viscoelastic properties of polymers*, John Wiley & Sons, New York, 1980.
14. Yang X.H., Zhu W.L. and Yan J.F.: J.Biomaterials Science. Polymer Edition *17*, 53 (2006).
15. Kamal M.R.: Polym.Eng.Sci. *14*, 23 (1974).

TERMOREOLOGICKÉ VLASTNOSTI VODNÉHO ZINKOVÉHO NÁTĚRU Z ROZTOKU KŘEMIČITANU SODNÉHO

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Při různé teplotě a úhlovém kmitočtu byla zaznamenána paměť dynamického smyku a ztrátové moduly G' a G'' vodního zinkového nátěru a jeho pojiva, roztoku křemičitanu sodného. Výsledky ukazují, že G' a G'' zpočátku klesají na minimum a poté začínají narůstat, přičemž teplota se pohybuje v intervalu od 5 do 95°C. Zinkový nátěr ani jeho pojivo ovšem nejsou reologicky jednoduché materiály.